

INORGANIC ARSENIC IN WORKPLACE ATMOSPHERES



Method Number:	ID-105
Matrix:	Air, Wipes (Smear Tabs), or Bulks
OSHA Permissible Exposure Limit:	0.01 mg/m ³
Collection Procedure:	Inorganic arsenic ¹ particulate in the air is collected by drawing a known volume of the air through a 0.8- μ m mixed-cellulose ester (MCE) filter and backup pad using a calibrated personal sampling pump. A chemically-treated backup pad is used if volatile inorganic arsenic species are suspected. If arsine is also suspected, a sampling train is used (see Section 5). Wipe and bulk materials are collected using grab sampling techniques.
Recommended Air Volume Ranges	
MCE Filter:	480 L to 960 L
Sampling Train (Section 5):	120 to 240 L
Recommended Sampling Rates	
MCE Filter:	2.0 L/min
Sampling Train (Section 5):	0.5 L/min
Analytical Procedure:	Air filters, backup pads, wipes (smear tabs), and bulks are digested with nitric acid and stabilized by addition of nickel. After digestion, a small amount of hydrochloric acid is added. Arsine collected on charcoal is extracted using a dilute nitric acid/nickel solution. All samples are then diluted to volume and analyzed by atomic absorption spectroscopy using a heated graphite atomizer.
Detection Limits	
Qualitative:	0.003 μ g/mL arsenic
Quantitative:	0.01 μ g/mL arsenic
Precision and Accuracy	
Validation Level:	0.006 to 0.04 mg/m ³
CV _T	0.10
Bias	+0.004
Overall Error	\pm 20%
Method Classification:	Validated Analytical Method
Chemist:	Steven Edwards
Date (Date Revised):	1982 (May, 1991)

¹ Inorganic arsenic means copper acetoarsenite and all inorganic compounds containing arsenic (except arsine) and measured as arsenic (8.1).

Commercial manufacturers and products mentioned in this method are for descriptive use only and do not constitute endorsements by USDOL-OSHA. Similar products from other sources can be substituted.

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1. Introduction

1.1 Scope

This method describes the collection and analysis of inorganic arsenic for airborne, wipe, and bulk material samples. Air samples can be taken for particulate and volatile inorganic arsenic. Sample preparation at the laboratory involves mineral acid digestion and nickel stabilization. The analysis is performed with an atomic absorption spectrometer (AAS) utilizing a heated graphite atomizer (AAS-HGA). Additional analytes (Cd, Cu, Fe, Pb, and Zn) can also be analyzed from the same sample media using flame AAS techniques.

In addition, samples previously prepared for ICP analysis by OSHA Method no. ID-125G (8.2) can also be determined for arsenic using the analytical technique described herein.

1.2 History

Previously, arsenic was analyzed at the OSHA Analytical Laboratory using an arsine generation procedure (8.3). The method required special gas generation equipment and was time-consuming. An early AAS-HGA method without the addition of nickel as a stabilizer was considered; however, this approach had decreased sensitivity, poor reproducibility, and was subject to potential interferences and loss of arsenic during analysis. The addition of nickel to samples minimizes these problems by the apparent formation of a stable nickel arsenide complex (8.4). This complex allows the use of a higher charring temperature during AAS-HGA analysis and minimizes interferences caused by incomplete volatilization of any organic substances contained in the sample matrix (8.5).

Compared to arsine generation, the AAS-HGA procedure offers the following advantages:

- 1) a simple digestion procedure,
- 2) increased ability to analyze other analytes from the same sample,
- 3) a decrease in sample loss and an increase in sample throughput.

1.3 Analytical Principle

This method uses a HGA with a Zeeman/L'vov configuration to analyze arsenic and reduce background contributions. Other background compensation techniques can be used.

1.3.1 The Zeeman electromagnet technique assists in minimizing background without the use of continuum sources such as the deuterium arc. A magnetic field is provided during the analytical atomization step and results in a "splitting" of the atom's energy levels. The capability of measuring the atomic absorption with and without the magnetic field applied during the atomization step provides a "clean" signal. This "clean" signal is the net difference between the signal produced with the magnetic field turned off and then on.

1.3.2 The L'vov platform is a pyrolytically-coated graphite support inserted into a graphite tube which is also pyrolytically-coated. This assembly offers a more uniform temperature distribution inside the graphite tube, increased sensitivity, and less opportunity for matrix effects from molecular formation and absorption during atomization.

1.4 Uses

Arsenic has metallurgical applications in industry where it is used for hardening lead and enhancing the toughness and corrosion resistance of copper. Arsenic compounds are used in medicine, glass manufacture, pigment production, rodent poisons, insecticides, fungicides, weed killers, semiconductor manufacture, and tanning processes.

1.5 Physical and Chemical Properties (8.6)

Metallic arsenic is a steel gray, brittle metal, with a density of 5.7. It also exists as yellow crystal, As₄, having a density of 2.0. Some physical properties of arsenic (CAS #7440-38-2) are:

Atomic weight	74.9216
Specific Gravity	5.727
Melting Point	sublimes without melting at 613 °C
Solubility	insoluble in H ₂ O; soluble in HNO ₃

2. Range and Detection Limit (8.7)

2.1 For this method, the working range is 0.01 to 0.5 µg/mL arsenic. For a 480-L air volume and 25-mL solution volume, this range permits quantitation without sample dilution from approximately 0.0005 to 0.03 mg/m³ arsenic.

2.2 Calculated quantitative detection limits (DL) are:

<u>Sample Type</u>	<u>Air Vol</u>	<u>Flow rate</u>	<u>Solution Vol</u>	<u>DL</u>
Air	480 L	2 L/min	25 mL	0.0005 mg/m ³
Air	120 L	0.5 L/min	10 mL	0.0008 mg/m ³
Wipe or Bulk	-----	-----	25 mL	0.25 µg

2.3 The range and detection limits of the other metal analytes (Cd, Cu, Fe, Pb, and Zn) should be unaffected by this sample preparation. Detection limits and analytical parameters for these and other elements can be found in references 8.2 or 8.8.

3. Precision and Accuracy

3.1 Previous and recent quality control samples (8.9.) containing arsenic in the approximate range of 0.5 to 4 times the OSHA PEL (assuming 960-L air volumes), gave the following data:

	<u>Sample Set #1</u>	<u>Sample Set #2</u>
Bias	-0.024	+0.004
CV	0.097	0.10
Overall analytical error	±21.8%	±20.0%
Analysis period	2/1982-4/1982	1/1989-12/1990
N	78	100
Analytical technique	HGA/D ₂	HGA/LD ₂ (5%) HGA/ZL (95%)

where: HGA/D₂ = Heated Graphite Atomizer with deuterium arc background correction.
HGA/LD₂ = Heated Graphite Atomizer/L'vov Platform with deuterium arc background correction.
HGA/ZL = Heated Graphite Atomizer with Zeeman/L'vov Platform

Approximately 95% of the samples from Set #2 were analyzed using the HGA Zeeman/L'vov platform approach mentioned in this method. The remaining samples were analyzed with a HGA/L'vov platform and deuterium arc background correction only. A significant difference in results was not noted.

3.2 Recovery data for arsenic analyzed in an "ICP digest" is presented in reference 8.7. No significant loss of arsenic was noted when using the "ICP digest" and a HGA equipped with a Zeeman/L'vov system.

3.3 For precision and accuracy data for other metals (Cd, Cu, Fe, Pb, and Zn) analyzed with arsenic, also see reference 8.7. Recoveries for these metals analyzed by flame atomic absorption were adequate.

4. Interferences

Sampling

Non-volatile organic arsenic-containing compounds will provide a positive interference when sampling for particulate arsenic. The industrial hygienist should make note of any organo-arsenic use in the area sampled.

Analysis

The analysis of arsenic in an "ICP-type digestion" matrix (8% HCl/ 4% H₂SO₄ as mentioned in reference 8.2) may require the use of significant background correction due to the contribution from sulfuric acid. In these cases, it is recommended to minimize background by using a Zeeman-type graphite furnace assembly with a L'vov platform inserted in pyrolytically-coated graphite tubes; other techniques can be used to diminish background effects provided they are evaluated using spiked samples and analytical recovery is adequate.

Perchloric acid (HClO₄) should not be used for sample digestions and subsequent analysis using this analytical technique. Inhibition of the arsenic signal after digestion of polyvinyl chloride filters and rapid graphite tube deterioration from HClO₄ have been noted (8.10).

5. Sampling

When other compounds or elements are known or suspected to be present in the sampled air, such information should be transmitted with the sample. Sampling for arsenic in air is dependent on the operation. If the operation being sampled has the potential for producing inorganic arsenic vapor and arsine, a sampling train (Sampling Media II) is used to capture the vapor and particulate. Some examples of operations potentially producing arsenic vapor are welding and torching (8.11). Arsine can be formed from arsenic when sufficient hydrogen is present with arsenic [i.e. lead-acid battery manufacturing plants (8.11)]. Sampling can be accomplished using one of two different approaches:

<u>Suspected Form</u>	<u>Sampling Media</u>	<u>Flow Rate (L/min)</u>
Particulate (+ Vapor)	I	2
Particulate + Vapor + Arsine	II	0.5

If possible, all samples should be taken for at least 240 min.

5.1 Equipment

5.1.1 Sampling Media I for particulate arsenic:

Mixed cellulose ester (MCE) filters (0.8 µm pore size), cellulose backup pads, and two- or three-piece cassettes, 37-mm diameter, (part no. MAWP 037 A0, Millipore Corp., Bedford, MA).

If volatile inorganic arsenic is suspected, the following is used:

For sampling particulate and volatile inorganic arsenic compounds (i.e., heated arsenic sources):

The cellulose backup pad is chemically treated and the pads and MCE filters are contained in three-piece cassettes. This chemical treatment ensures capture of volatile inorganic arsenic in the backup pad (8.11). The backup pads are treated using an impregnation solution:

Pipettes, 0.5 mL

Sodium carbonate (Na₂CO₃)

Glycerol (C₃H₈O₃)

Impregnation solution [Na₂CO₃ solution with glycerol] - prepare by dissolving 4.0 g Na₂CO₃ in 50 mL deionized water, add 2 mL glycerol, and dilute this solution to 100 mL with deionized water.

Remove filters from the three-piece cassettes and use the opened cassettes as supports for backup pad impregnation. Each backup pad should be resting on the ridge of the middle insert of the cassette and not in contact with the cassette base. Slowly pipette 0.5 mL of the impregnation solution over the entire backup pad, let dry overnight, and then place the MCE filters on top of the backup pads and assemble the cassettes.

5.1.2 Sampling Media II (for sampling when arsine is also suspected to be present):

Sampling media I with the chemically treated backup pad is used in series with an arsine sampling tube. This tube is composed of glass and contains 400 mg (front) and 200 mg (backup) sections of activated coconut shell charcoal. This sampling train is necessary if volatile inorganic arsenic species and arsine are suspected to be present in the air.

5.1.3 Sampling pumps capable of sampling at 2 L/min (Sampling Media I) or 0.5 L/min (Sampling Media II).

5.1.4 Assorted flexible tubing.

5.1.5 Stopwatch and bubble tube or meter for pump calibration.

5.1.6 Gel bands (Omega Specialty Instrument Co., Chelmsford, MA) for sealing cassettes.

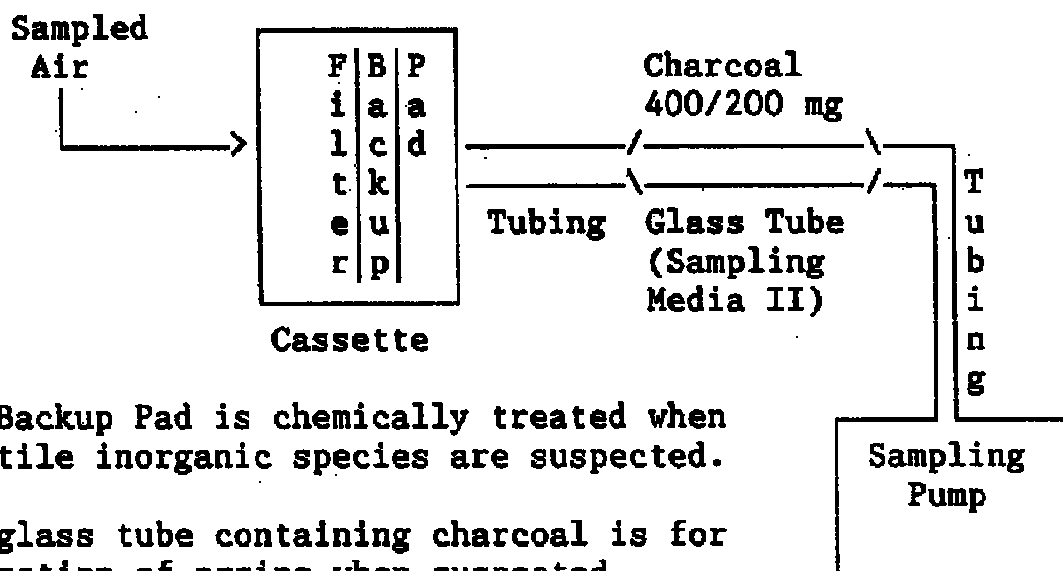
5.1.7 Scintillation vials, 20 mL, (part no. 74515 or 58515, Kimble, Div. of Owens-Illinois Inc., Toledo, OH) with polypropylene or Teflon cap liners. If possible, submit bulk or wipe samples in these vials.

5.1.8 Smear tabs, (Whatman 50, part no. 225-24, SKC Inc., Eighty Four, PA) for wipe sampling.

5.2 Sampling Procedure - Air Samples

5.2.1 Place an MCE filter and a cellulose backup pad in each two- or three-piece cassette. The backup pad should be chemically-treated if volatile inorganic arsenic compounds are suspected. Seal each cassette with a gel band.

5.2.2 Attach calibration sampling media to the pump using flexible tubing. Depending on the sampling media in use, follow the sampling scheme shown:



The Backup Pad is chemically treated when volatile inorganic species are suspected.

The glass tube containing charcoal is for collection of arsine when suspected.

If arsine is suspected, use a minimum amount of tubing to connect the cassette to the arsine sampling tube.

5.2.3 Calibrate each personal sampling pump with prepared sampling media in-line to within $\pm 10\%$ of the recommended flow rate of 2 L/min (Sampling Media I) or 0.5 L/min (Sampling Media II). Remove the calibration media and attach new sampling media to the calibrated pump.

5.2.4 Place the sampling media/pump assembly in appropriate positions on the employee or the workplace area.

5.2.5 If possible, collect full-shift samples. The minimum recommended air volume is 480 L (120-L for Sampling Media II). Take samples to cover the workshift.

5.2.6 If the filter becomes overloaded while sampling, prepare and use another filter cassette. Take consecutive samples using shorter sampling periods if overloading occurs.

5.2.7 Place plastic end caps on each sampling media after sampling.

5.3 Sampling Procedure - Wipe Samples

5.3.1 Wear clean, impervious, disposable gloves when taking each wipe sample.

5.3.2 Moisten the wipe filters with deionized water prior to use.

5.3.3 If possible, wipe a surface area covering 100 cm².

5.3.4 Fold the wipe sample with the exposed side in.

5.3.5 Transfer the wipe sample into a 20-mL scintillation vial and seal with vinyl or electrical tape.

5.4 Sampling Procedure - Bulk Samples

In order of laboratory preference, bulk samples may be one of the following:

- 1) a high-volume filter sample,
- 2) a representative settled dust (rafter) sample,
- 3) a sample of the bulk material in the workplace.

Transfer the bulk material into a 20-mL scintillation vial and seal with vinyl or electrical tape.

5.5 Shipment

5.5.1 Submit at least one blank sample with each set of air, charcoal, or wipe samples. Blank samples should be handled in the same manner as other samples, except that no monitoring is performed with these samples.

5.5.2 Attach an OSHA-21 seal around each cassette, scintillation vial, and glass tube (if used) in such a way as to secure the end caps. Document the industrial operation(s) the samples were taken from. Send the samples along with any blank samples to the laboratory with the OSHA-91A paperwork requesting arsenic analysis. Also note whether volatile arsenic or arsine was suspected and which Sampling Media was used.

5.5.3 If desired, specify other elements of interest. At the OSHA Technical Center the following elements are analyzable on the same filter, wipe, or bulk with arsenic:

<u>Technique</u>	<u>Element</u>
Atomic Absorption	Cd, Cu, Fe, Pb, Zn
ICP	Be, Cd, Cr, Co, Cu, Fe, Mn, Mo, Ni, Pb, Sb, V, Zn

Choose any combination of three elements listed for Atomic Absorption or choose arsenic/ICP analysis if more than three elements are desired.

5.5.4 The type of bulk sample should be stated on the OSHA-91A and cross-referenced to the appropriate air sample(s).

5.5.5 Ship bulk samples separately from air samples. They should be accompanied by Material Safety Data Sheets, if available. Check current shipping restrictions and ship to the laboratory by the appropriate method.

6. Analysis

6.1 Safety Precautions

6.1.1 Arsenic is considered a human carcinogen (8.1, 8.6). Use extreme care when handling arsenic or arsenic-containing compounds.

6.1.2 All work with concentrated acids is potentially hazardous. Care should be exercised when handling any acidic solutions. Acid solution contact with work surfaces should be avoided. If any acid contacts the eyes, skin, or clothes, flush the area immediately with copious amounts of water. Medical treatment may be necessary.

6.1.3 Always wear safety glasses and protective clothing when using chemicals. Prepare all mixtures, samples, or dilutions in an exhaust hood. To avoid exposure to acid vapors, do not remove any beakers from the hoods until they have returned to room temperature and have been diluted.

6.1.4 Use a pipette bulb, never pipette by mouth.

6.1.5 When scoring glass sampling tubes to remove the sorbent before analysis, score with care. Apply only enough pressure to scratch a clean mark on the glass. Use a paper towel or cloth to support the opposite side while scoring. Moisten the mark with DI H₂O and wrap the tube in cloth before breaking. If the tube does not break easily, re-score. Dispose of glass in a waste receptacle specifically designed and designated for broken-glass.

- 6.1.6 Consult the Standard Operating Procedure (SOP)(8.12) and any instrument manuals before using any instrument.
- 6.1.7 Since metallic elements and other toxic substances are vaporized during HGA operation, it is imperative that an exhaust hood is installed and used directly above the graphite furnace. Always ensure the exhaust system is operating before proceeding with the analysis.
- 6.1.8 Do not look directly at the furnace during the atomization step or at the emission of an electrodeless discharge lamp.

6.2 Equipment

6.2.1 Atomic absorption spectrophotometer consisting of a(an):

- a) Heated graphite furnace atomizer with argon purge system and graphite tubes

Note: If samples are analyzed in matrices other than recommended in this method (4% HNO₃, 200 µg/mL Ni), or matrix-matching samples and standards is difficult, it is recommended to use an HGA capable of significant resolution of background, such as a Zeeman/L'vov Platform-type HGA (Perkin-Elmer, Norwalk, CT) with pyrolytically-coated graphite tubes.

- b) Pressure-regulating devices capable of maintaining constant argon purge pressure.
- c) Optical system capable of isolating the desired wavelength of radiation.
- d) Adjustable slit.
- e) Light measuring and amplifying device.
- f) Display, strip chart, or computer interface for indicating the amount of absorbed radiation.
- g) Deuterium Arc Background Corrector (if Zeeman background correction is unavailable).
- h) Electrodeless Discharge Lamp (EDL) for arsenic and an EDL power supply (Note: A modulated system is necessary when using a Zeeman HGA.).
- i) Automatic sampler.

6.2.2 Glassware

- a) Phillips beakers, 125- and 250-mL
- b) Volumetric flasks, Class A: 10-, 25-, 50- and 100-mL
- c) Pipettes, Class A: Assorted sizes
- d) Scintillation vials, 20-mL (for desorbing charcoal)

6.2.3 Forceps.

6.2.4 Exhaust hood and hotplate, or microwave digestion system (model no. MDS-81, CEM Corp., Matthews, NC).

6.2.5 Filtering apparatus consisting of MCE filters, 0.45-µm pore size, 47-mm diameter (cat. no. HAWP 047 00, Millipore Corp., Bedford, MA) and filtering apparatus (cat. no. XX15 047 00, Millipore).

6.2.6 Automatic pipets, adjustable, 0.1 to 5.0 mL range (models P-1000 and P-5000, Rainin Instruments Co., Woburn, MA).

6.2.7 Glass tube scorer, or needle, 21 to 25 gauge - for glass wool, foam, and sorbent from glass tubes. A piece of bent wire can also be used.

6.2.8 Exhaust vent.

6.2.9 Ultrasonic bath (for arsine samples).

6.2.10 Analytical balance (0.01 mg).

6.2.11 Arsine sampling media (for standard preparation if arsine has been collected): Obtain six sampling tubes each containing 400 mg (front) and 200 mg (backup) sections of activated coconut shell charcoal.

6.3 Reagents (All chemicals should be reagent grade or better.)

6.3.1 Deionized water (DI H₂O) with a specific conductance of less than 10 µS.

6.3.2 Mineral acids (used for digestions and dilution solution preparation)

CAUTION: Refer to Sections 6.1.2-6.1.3 before using acids.

- a) Hydrochloric acid (HCl), concentrated (36.5 to 38%).
- b) Nitric acid (HNO₃), concentrated (69 to 71%).

6.3.3 Mineral acids (used for cleaning glassware)

CAUTION: Refer to Sections 6.1.2.-6.1.3. before using acids.

- a) Nitric acid, 1:1 HNO₃/DI H₂O mixture: Carefully add a measured volume of concentrated HNO₃ to an equal volume of DI H₂O.
- b) Nitric acid 10% v/v: Carefully add 100 mL of concentrated HNO₃ to 500 mL of DI H₂O and then dilute to 1 L.

6.3.4 Nickelous nitrate [Ni(NO₃)₂·6H₂O].

6.3.5 Stabilizer, 1,000 µg/mL Ni solution - Dissolve 5.0 g nickelous nitrate in 100 mL of DI H₂O, add 5 mL concentrated HNO₃, and dilute to 1-L with DI H₂O.

6.3.6 Mixed cellulose ester (MCE) filters, 0.8-µm pore size, 37-mm diameter.

(Note: These filters are used for matrix-matching standards with samples. If possible, use the same brand and lot of filters for air sampling and matrix-matching.)

6.3.7 Diluting solution: Place 20 blank MCE filters in a cleaned 250-mL Phillips beaker and carefully add 100 mL of concentrated HNO₃ and 100 mL of the 1,000 µg/mL nickel solution. Digest this mixture on a hot plate until about 20 to 40 mL of solution remain. Transfer the solution to a cleaned 500-mL volumetric flask, add 2 mL of concentrated HCl, and dilute to volume with DI H₂O.

6.3.8 Standard solution, 1,000 µg/mL arsenic: If possible, use commercially available aqueous standards. Observe expiration dates; if none, properly dispose the standard after 1 year.

6.3.9 If a commercial standard (Section 6.3.8) is not available, a 1,000 µg/mL solution can be prepared as follows:

- 1) Sodium hydroxide (NaOH).
- 2) Arsenic trioxide (As₂O₃).
- 3) Sodium hydroxide, 10% solution: Dissolve 10 g of NaOH in about 75 mL of DI H₂O. Dilute to 100 mL.

In a cleaned 1-L volumetric flask, dissolve 1.320 g As₂O₃ in 25 mL 10% NaOH. Dilute to volume with DI H₂O, and mix. Dispose of properly after 1 year.

6.3.10 Argon, compressed gas (for HGA tube purges).

6.4 Glassware Preparation

6.4.1 Place the Phillips beakers in an exhaust hood and add approximately 10 mL of a 1:1 HNO₃/DI H₂O mixture in each 125- or 250-mL Phillips beaker. Using a hot plate, apply moderate heat to the beakers until refluxing occurs. Carefully decant the acid mixture into a waste container and allow the beakers to cool before removing from the hood. Rinse the beakers thoroughly with DI H₂O.

6.4.2 Rinse all volumetric flasks with 10% v/v HNO₃ and then rinse thoroughly with DI H₂O.

6.4.3 Allow all glassware to air dry before proceeding.

6.5 Standards

6.5.1 Dilute stock solutions:

Prepare dilute arsenic stock solutions (0.1-, 1-, and 10- $\mu\text{g}/\text{mL}$) by diluting aliquots of the 1,000- $\mu\text{g}/\text{mL}$ standard solution with DI H_2O . Prepare the diluted stock solutions on the same day the working standards are prepared.

6.5.2 Working standards:

A dilution scheme using 0.1-, 1-, and 10- $\mu\text{g}/\text{mL}$ stock solutions is proposed below.

Working Standard ($\mu\text{g}/\text{mL}$)	Stock Solution ($\mu\text{g}/\text{mL}$)	Stock Solution (mL)	Final Volume* (mL)
0.01	0.1	10	100
0.02	0.1	20	100
0.5	1	5	100
0.1	1	10	100
0.2	10	2	100
0.5	10	5	100

*Diluent is the diluting solution (Section 6.3.7)

Dilute all working standards to volume using the diluting solution. This will assure the matrix (acid, sample filter, and nickel content) of the samples (air and wipe) and standards are closely matched. Dispose working standards after 6 months.

6.5.3 Standards for arsine determinations

Remove the 400-mg section of charcoal sorbent from six arsine sampling tubes. Place each 400-mg section in a separate vial. Pipet a 3-mL aliquot from each working standard (prepared in Section 6.5.2.) into each vial such that six standards ranging in concentration from 0.01 to 0.5 $\mu\text{g}/\text{mL}$ arsenic are prepared with a charcoal matrix.

6.6 Sample Preparation

Note: Always prepare blank samples with every sample set. Prepare an additional blank media sample any time an extra procedure is used (i.e. wiping out the particulate contained inside a cassette with an MCE filter or preparing a contaminated backup pad). If possible, this blank media should be from the same manufactured lot as the prepared filter, tube, or backup pad.

6.6.1 Preparation of air and wipe sample filters

- 1) Open the filter cassette or scintillation vial, carefully remove the sample filter with forceps, and place in a labeled Phillips beaker. Use 125-mL beakers for air samples and smear tabs. If the cassette or vial contains loose dust, carefully rinse the dust into the beaker with DI H_2O . If necessary, wipe out the dust with a clean MCE filter and place this filter in the sample beaker.
- 2) Prepare and analyze backup pads if:
 - a) volatile inorganic arsenic species are suspected, or
 - b) the backup pad appears to be discolored. Discoloration may be due to leakage of air around the filter during sampling.

If analysis of the backup pad is necessary, place each backup pad in a separate beaker.

6.6.2 Preparation of bulk samples

- 1) Review any available material safety data sheets to determine safe bulk handling. The data may also offer a clue regarding the aliquot amount needed for adequate detection.
- 2) Measure by volume or weight an appropriate aliquot of any liquid bulk sample. Weigh the appropriate amount of any solid bulk sample.

Note: Aliquot amounts of bulks are dependent on the analytical sensitivity, detection limit, and solubility of the material used. If uncertain, a 20- to 50-mg aliquot of a solid material can be taken as a starting point. Make sure the aliquot taken is representative of the entire bulk sample. If necessary, use a mortar and pestle to grind any nonhomogenous particulate bulk samples in an exhaust hood.

After measuring, transfer the aliquot to a 250-mL Phillips beaker.

6.6.3 Preparation of arsine (charcoal) samples

- 1) Score the tube with a glass tube cutter (also see Section 6.1.5.) and then break open the front section of the tube above the glass wool. An alternative approach to scoring and breaking is to carefully remove the glass wool with a bent wire or needle.
- 2) Carefully transfer each section of the sorbent to separate 20-mL scintillation vials without losing any particles.

6.7 Sample Digestion or Extraction

6.7.1 MCE air filters and smear tabs

Place the beakers in an exhaust hood and carefully add 3 to 5 mL concentrated HNO₃ and the appropriate amount of Stabilizer (Section 6.3.5.) as shown below. Place the beakers on a hot plate and heat the samples until the appropriate amount of solution remains as shown below.

<u>Air Vol (L)</u>	<u>Stabilizer (mL)</u>	<u>Digestion Vol (mL)</u>
< 200	2.0	0.5
≥ 200	5.0	1.0
Smear tabs	5.0	1.0

Note: If the sample solution is not clear, add a second portion of approximately 1 to 2 mL of concentrated HNO₃. Apply heat until the appropriate digestion volume listed above remains.

Remove the beakers from the hotplate. Allow beakers to cool, then add 100 µL (~2 drops) of HCl to each and swirl the contents.

6.7.2 Polyvinyl chloride filters, or backup pads

Note: Polyvinyl chloride (PVC) filters are not routinely used for arsenic sample collection and analysis. In some cases the industrial hygienist will sample for total or respirable dust using PVC filters and also submit these samples for analysis. The PVC filter will not be completely digested using the acid digestion listed in this method; rather, the particulate is acid-extracted from the filter.

Perchloric acid should not be used to digest arsenic samples collected on PVC filters or backup pads; low recoveries for arsenic were noted when PVC filters were digested using an H₂SO₄/HCl/HClO₄ acid matrix (8.10). In addition, graphite tube degradation is greatly accelerated from perchloric acid.

Place the beakers in an exhaust hood and add the following amount of concentrated HNO₃ to the beakers:

Backup pads	10 to 15 mL
PVC filters	3 to 5 mL

Follow the digestion procedure mentioned above Section 6.7, MCE air filters and smear tabs and determine the amount of Stabilizer needed, and digestion volumes. After heating on a hot plate and subsequent cooling, each PVC filter should be thoroughly rinsed with DI H₂O during quantitative transfer of the sample solution.

6.7.3 Bulk samples

If necessary, use a microwave digestion system to facilitate digestion [For further information regarding microwave digestion, see the Microwave Standard Operating Procedure (8.13)].

Add 10 to 30 mL HNO₃, 5 mL of Stabilizer, and place the beaker on a hot plate. Digest the bulk sample until the material dissolves and approximately 1 mL of solution remains. Remove the beakers from the hot plate. Allow beakers to cool, then add 40 µL (~2 drops) of HCl to each and swirl the contents.

6.7.4 Arsine (charcoal) samples

To each scintillation vial add 3 mL of Stabilizer solution (Section 6.3.5). Cap and sonicate each vial contents for 10 min.

6.7.5 Filtration - any solutions samples containing particulate

Digested samples: If particulate matter is present after digesting, allow the sample to cool, add approximately 10 mL DI H₂O, then filter the solution through a 0.45-µm MCE filter. Save the filtrate for analysis. Repeat the digestion procedure above for the filter containing the particulate.

Arsine samples: If particulate is present after extraction (i.e. charcoal fines), filter the 3-mL solution through a 0.45-µm MCE filter, and analyze the filtrate.

6.7.6 Dilution - all samples

Digested samples: Allow all beakers to cool to room temperature in an exhaust hood before proceeding. Carefully add about 5 mL of DI H₂O to each beaker, rinsing down the insides of each beaker. Quantitatively transfer each sample solution to individual volumetric flasks. Dilute to volume with DI H₂O and mix well. Recommended final sample solution volumes are:

Air (≥200-L), wipe, and bulk samples	25 mL
Air volumes <200-L	10 mL

Larger dilution volumes can be used for bulk samples; however, the final solution volume should contain 4% HNO₃ and 200 µg/mL Ni.

Arsine samples: For charcoal samples, further dilution is not necessary.

6.7.7 Samples previously prepared for ICP analysis

For samples already prepared and analyzed using OSHA Method no. ID-125G, no additional sample preparation is necessary.

6.8 Instrument Setup and Analysis

6.8.1 Set up the spectrometer and HGA according to the SOP (8.12.) or the manufacturer's instructions. Suggested parameters for two specific instruments are shown in Appendix A.

- 1) Install an EDL for arsenic and allow to stabilize.
- 2) Optimize conditions such as lamp position, furnace alignment, etc. as mentioned in the SOP (8.12).
- 3) Be sure cooling water is circulating around the furnace before heating it and if deuterium (D2) arc background correction is used, assure the purge air is circulating around the D2 components before lighting the D2 lamp.

4) Only for those samples previously prepared using OSHA Method ID-125G:

Set up the instrument such that a nickel spike is added to each sample or standard immediately prior to HGA initiation. A 10- μ L aliquot of the sample can be injected, then overlay 5 μ L of Stabilizer (Section 6.3.5) on the sample before starting the HGA cycle. Standards prepared in Section 6.5 can be used during analysis of these samples.

- 6.8.2 Inject an aliquot of a standard into the HGA and measure the absorbance of the standard using peak height or area. The standard concentration should be within the linear range. If possible, compare this absorbance to a value from a previous analysis. Measure other prepared working standards first to assure proper instrument operation.
- 6.8.3 Analyze samples and blanks. Analyze a standard after every four or five samples. Standards should bracket the sample concentrations. Standard readings should be within 10 to 15% of the readings obtained at the beginning of the analysis.
- 6.8.4 If any samples exceed the linear range, dilute with diluting solution (Section 6.3.7) to bring them into the working range.
- 6.8.5 Cadmium, copper, iron, lead, and zinc can be analyzed in conjunction with the arsenic analysis using an atomic absorption spectrophotometer (air/acetylene flame) and direct aspiration. Analytical conditions for flame analysis of these elements are shown in Appendix B. Additional information can be found in OSHA Method No. ID-121 or instrument manufacturers' manuals.

6.9 Analytical Recommendations

- 6.9.1 The amount of nickel added to each sample can vary slightly from the standards without producing a significant matrix effect. An excess of nickel always needs to be present. (Note: A common range is to have from 100 to 2,000 μ g/mL Ni present in the samples and standards.)
- 6.9.2 When standards are prepared, analyze the old and new standards and compare results to verify the new standard is correct. If two or more 1,000 μ g/mL arsenic solutions are available for standard preparations, rotate the preparation from one stock solution to the next to verify the quality.
- 6.9.3 Keep a permanent record of all standard preparation and comparison data. Assign and follow expiration dates for all standards.
- 6.9.4 Always analyze blank samples along with the other samples. Treat blanks in the same fashion as samples, including any filtration steps.
- 6.9.5 If possible, analyze quality control samples from an independent source. The quality control samples should be freshly prepared if they are derived from liquid spikes on MCE filters.

7. Calculations

If sample or standard injection volumes are not constant, the differences need to be considered before establishing a curve and calculating results.

- 7.1 Plot the peak height or area versus the standard concentrations in μ g/mL. Using a least squares method, determine the equation for the best curve fit.
- 7.2 Use the equation to calculate the concentration of arsenic in μ g/mL for each sample.
- 7.3 Calculate the concentration of each air sample as:

where: $C = \text{arsenic (mg/m}^3\text{)}$

$$C = \frac{(A \times SA \times D) - (B \times SB)}{\text{Air Vol}}$$

A = concn of arsenic in the sample solution (μ g/mL)
B = concn of arsenic in the blank solution (μ g/mL)
SA = sample solution volume (mL)
SB = blank solution volume (mL)

D = sample dilution factor (if any)
Air Vol = air volume sampled (L)

- 7.4 For wipe or bulk samples, calculate the total amount (in µg) of analyte in each sample using the equation above without air volumes. Convert bulk sample analytes to % composition using:

where: C =
arsenic amount (µg) **Arsenic %(w/w)** = $\frac{C \times 100\%}{(\text{Sample wt})(1000 \mu\text{g}/\text{mg})}$ (Bulk Samples)

Sample wt = aliquot (in mg) of bulk taken in Section 6.6.

- 7.5 Analytes other than arsenic are calculated in the same fashion as described above. For the charcoal sampling media results from Sampling Media II, multiply the arsenic found by 0.326 to obtain ppm arsine values. For air samples, multiply any results for zinc or iron by the appropriate gravimetric factor (ZnO/Zn = 1.2447, Fe₂O₃/Fe = 1.4298).
- 7.6 With the exception of arsine sample results, combine results from sampling trains or filtrate/particulate samples to give a single arsenic result per sample. As examples:

<u>Total As exposure</u>	<u>Results</u>
Sampling Media I or II	= filter + backup pad*
Samples containing undigested particulate	= filtrate + redigest

*If the chemically-treated pad was used or if the air sample leaked onto the pad.

- 7.7 Reporting Results to the Industrial Hygienist

7.7.1 Report air sample results as mg/m³ arsenic.

7.7.2 Report wipe sample concentrations as total micrograms or milligrams arsenic.

7.7.3 Report bulk sample results as approximate percent by weight arsenic (Note: Sample results for bulk liquids may be reported as approximate percent by volume if volumetric aliquots were taken during sample preparation.) Due to differences in sample matrices between bulks and standards, bulk results are approximate.

Analytes other than arsenic are reported in the same fashion as described above. Arsine results (in ppm) are reported separately. Air sample results for zinc and iron are reported to the industrial hygienist as oxides.

8. References

- 8.1 "Inorganic arsenic," Code of Federal Regulations 29 CFR 1910.1018. 1989. 142-155.
- 8.2 Occupational Safety and Health Administration Technical Center: Metal and Metalloid Particulate in Workplace Atmospheres (ICP) by J. Septon (USDOL/OSHA-SLTC Method No. ID-125G). Salt Lake City, UT. Revised 1991.
- 8.3 Occupational Safety and Health Administration Analytical Laboratory: OSHA Manual of Analytical Methods edited by R.G. Adler (Method No. I-2). Salt Lake City, UT. 1978.
- 8.4 Ediger, R.D.: Atomic Absorption Analysis with the Graphite Furnace using Matrix Modification. Atomic Absorption Newsletter 14(5): 127-130 (1975).
- 8.5 Edwards, S.E.: "The Determination of Arsenic and Lead on a Single Personal Air Sample." Paper presented at American Industrial Hygiene Association National Conference, Houston, TX, 1980.
- 8.6 Hawley, G.G.: The Condensed Chemical Dictionary. 11th ed. New York: Van Nostrand Reinhold Co., 1987.
- 8.7 Occupational Safety and Health Administration Technical Center: Arsenic Backup Data Report (ID-105). Salt Lake City, UT. 1991.
- 8.8 Occupational Safety and Health Administration Technical Center: Metal and Metalloid Particulate in Workplace Atmospheres (Atomic Absorption)(USDOL/OSHA-SLTC Method No. ID-121). Salt Lake City, UT. Revised 1990.

- 8.9 Occupational Safety and Health Administration Technical Center: OSHA Laboratory Quality Control Division Data by B. Babcock. Salt Lake City, UT, 1990 (unpublished).
- 8.10 Occupational Safety and Health Administration Analytical Laboratory: As on FWSB filters by ICP digest by C. Merrell. Salt Lake City, UT. 1989 (unpublished).
- 8.11 Costello, R.J., P.M. Eller, and R.D. Hull: Measurement of Multiple Inorganic Arsenic Species. Am. Ind. Hyg. Assoc. J. 44(1): 21-28 (1983).
- 8.12 Occupational Safety and Health Administration Technical Center: AAS-HGA Standard Operating Procedure. Salt Lake City, UT. In progress (unpublished).
- 8.13 Occupational Safety and Health Administration Analytical Laboratory: Standard Operating Procedure for Microwave Digestions. by D. Cook. Salt Lake City, UT. 1989 (unpublished).

Appendix A

Instrument	Typical Instrument Parameters*	
	Zeeman*	PE 5000*
Wavelength ⁺	197.3 nm	197.3 nm
Slit	0.7 nm	0.7 nm low
Signal Mode	Peak Area	Peak Area
D ₂ Background Correction		AA-BG/ABS
Integration Time	6 s	Yes
Sample Injection Vol	10 µL	6 s
Automatic sampler	AS60**	10 µL
		AS40**

Zeeman* or PE 5000* with L'vov Platform

		Furnace	Time		Internal
		Temperature (°C)	Ramp (s)	Hold (s)	Argon Flow (mL/min)
1)	Pre-dry	90	5	10	300
2)	Dry	140	30	10	300
3)	Char	1300	10	20	300
4)	Cool Down	30	1	8	300
5)	Atomize	1300	0	5	0
6)	Burn out	2600	1	6	300

* Instruments are:

Zeeman = Model 5100 Zeeman Atomic Absorption Spectrophotometer equipped with a model 600 HGA controller (Perkin-Elmer, Norwalk, CT)

PE 5000 = Model 5000 Atomic Absorption Spectrophotometer equipped with a model 500 HGA controller (Perkin-Elmer)

** Model numbers of automatic samplers (Perkin-Elmer)

+ Secondary wavelength is used to increase the upper linear range. Primary wavelength of 193.7 nm can be used to increase sensitivity; however, a decrease in the upper range may be noted.

Appendix B

Cd, Cu, Fe, Pb, Zn Analysis

The following parameters were used for the validation (8.7.)(atomic absorption-air/acetylene flame) of Cd, Cu, Fe, Pb, and Zn:

Metal	Wavelength (nm)	Slit Setting (nm)	Light Source	Comments
Cd	228.8	0.7	HCL	
Cu	324.7	0.7	HCL	
Fe	248.3	0.2	HCL	**
Pb	283.3	0.7	HCL	
Zn	213.9	0.7	HCL	

HCL = Hollow Cathode Lamp

** When Fe is determined in the presence of Ni and HNO₃, a reduction in sensitivity is observed. This effect can be controlled by using a very lean (hot) flame.

All analytes were analyzed using an oxidizing air/acetylene (lean-blue) flame.